CHARACTERIZATION OF ANODIC BISMUTH OXIDE FILMS

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The electrochemistry of "valve" metals (Al, Ti, Zr, Ta, Bi, etc.) has been extensively studied due to their applications in optical films, microelectronics, capacitor manufacturing and protection against corrosion. Among valve metals, bismuth occupies a special place since bismuth oxide films show electrical rectification [1-3]. Previous studies on the properties of bismuth oxide by means of EIS have been made in terms of the semiconducting and dielectric properties of Bi_2O_3 films grown under potentiodynamic or potentiostatic conditions [4].

In this work the anodic growth of bismuth oxide films electroformed under potentiodynamic or galvanostatic conditions as well as their stability in the formation electrolyte were studied. Bismuth oxide films of different thickness were grown potentiostatically or galvanostatically up to different potential values and EIS measurements were performed at the open circuit potential employing an Impedance Spectrum Analyzer Zahner IM5d in the 10 mHz-1 MHz frequency range. The working electrode consisted of a polycrystalline bismuth rod (99.999% purity) polished with emery paper, diamond paste (9 μm) and alumina (0.05 μm). Measurements were performed in NaOH, H_2SO_4 or buffered phosphate solutions of different concentration and pH. Ellipsometry in situ was used as a monitoring technique during the anodic growth of the anodic oxide films as well as during the measurements at the open circuit potential in the formation electrolyte. Ellipsometric measurements were made in a Rudolph Research 2000 FT rotating analyzer automatic ellipsometer. The wavelength employed was 546.1 nm with the incident light beam at 70º.

Impedance data for anodic oxide films of different thickness were interpreted in terms of equivalent electric circuits employing different models (single or duplex films, space-charge region, porous layers, etc). For films grown in strongly alkaline NaOH solutions, log /Z/ as well as phase angle *vs.* frequency data show the presence of two time constants. The fitting process allow us to explain the behaviour obtained with a model consisting of a very thin nonporous barrier layer and a thick porous outer layer [5,6], although for very thin films the influence of the space-charge region can be important. The values of C^{-1} as well as the resistance obtained for the inner barrier layer follows a linear dependence with potential as expected for a dielectric material. On the other hand, the ellipsometric experiments obtained during the anodic growth and the circuit openings for taking the EIS measurements, show both a change in the optical properties and a decrease of film thicknes with time due to chemical dissolution and change in porosity of the outer layer during dissolution. For films grown up to different potential values in nearly neutral phosphate solutions, the impedance spectra can be fitted with the described model although in this case the inner layer is thick and the outer layer is thin and its thickness remains practically constant with potential. On the contrary, both C^{-1} and R for the inner layer increase steadily with potential up to *ca.* 9V. The ellipsometric experiments obtained during the anodic growth and the circuit openings for taking the EIS measurements, shows only a slight change in optical properties and the Ψ - Δ response for the growth can be fitted in the whole thickness range by means of a single film model with optical anisotropy of the oxide [7] from which the optical constants as well as the film thickness (d) can be determined. From the C^{-1} - E and d - E relationships, results a value of 9.2×10^5 Vcm^{-1} for the growing field as expected for oxide growth by a "high field" mechanism.

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